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2nd International Workshop on Spin and Orbital Magnetism in Actinides

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2^{nd} International Workshop on Spin and Orbital Magnetism in Actinides

Abstract Book

Chair:	J.G. Tobin, LLNL
Co-Chair:	D.K. Shuh, LBNL
Conf. Secy:	K. Copp, LLNL

Claremont Resort and Spa
Berkeley, CA, USA
October 13-15, 2002

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We gratefully acknowledge financial sponsorship for this meeting from the Enhanced Surveillance Campaign at Lawrence Livermore National Laboratory and contributions from the Chemical Sciences Division of Lawrence Berkeley National Laboratory.

Sunday, October 13

5:00 PM	**Reception and Opening Poster Session**
8:00 PM	**End**

Monday, October 14

8:00 AM	**Welcome**
8:10 AM	**Session I: Theoretical Overview and Recent Developments**
8:10 AM	B. Johansson, "Magnetic, Structural and Electronic Relationshipsbetween the Lanthanide and Actinide Elements"
8:50 AM	G. Kotliar, "Dynamical Mean Field Theory of Elemental Plutonium"
9:30 AM	A.McMahan, "Thermodynamic and spectral properties of compressed Ce calculated by the merger of LDA and DMFT"
10:10 AM	**Break**
10:30 AM	**Session II: Photoelecton Spectroscopy of Pu and Pu Mat'ls**
10:30 AM	T. Gouder, "5f Localization in Ultrathin Pu Layers"
11:10 AM	J. Joyce, "Electronic Structure of Pu and Pu Compounds from PES"
11:50 PM	**Lunch**
1:00 PM	J. Tobin, "A New Paradigm for the Determination of 5f Electronic Structure using Spin-Dependent Photoelectron Spectroscopy"
1:40 PM	G. van der Laan, "Core-level photoemission spectra as a tool to assess the 5f electron localization of alpha and delta-like Pu"
2:20 PM	**Session III: Poster Viewing with Refreshments**
4:00 PM	**Session IV: Resistivities and Susceptibilities**
4:00 PM	J.-M. Fornier, "Magnetic properties of PuAm solid solutions : evidence for a Curie-Weiss behavior and aging effects"
4:40 PM	L. Havela, "Non-Fermi Liquid Behavior in a Band Metamagnet UCoAl"
5:20 PM	M. Fluss, "Temperature Dependent Properties of Defects from Ion-Irradiation in Pu(Ga)"
6:00 PM	**End**
7:00 PM	**Dinner** W. Nellis, " Metallization of Hydrogen"

Tuesday, October 15

8:00 AM	**Session V: X-ray and Neutron Measurements, Analysis and Simulations**
8:00 AM	N. Edelstein, "Interplay of the spin-orbit and crystal field interactions of fn ions in crystals"
8:40 AM	G. Lander, "NpO2 : resonant x-ray scattering casts new light on an old problem"
9:20 AM	K. McEwen, "Quadrupolar and magnetic phase transitions in UPd3"
10:00 AM	**Break**
10:30 AM	M. Brooks, "Theory of Ground State Spin and Orbital Moments with Screened Exchange Interactions"
11:10 AM	L. Soderholm, "Correlated Electron Behavior in a Eu-exchanged W-O cluster"
11:50 PM	**Lunch**
1:00 PM	**Session VI: Pu Theory**
1:00 PM	P. Soderlind, "Density-functional investigation of magnetism in delta-Pu"
1:40 PM	J. Wills, "A mixed-level model of orbital and spin correlation in actinide materials"
2:20 PM	**Break**
2:50 PM	B. Sadigh, "First-Principles Calculations of the alpha and delta phases in Pu and Pu-Ga"
3:30 PM	A. Kutepov, "The ab-initio magnetic moments of alpha-plutonium"
4:10 PM	**Session VII: Workshop Summary and Discussion**
5:00 PM	**End**

Session I: Theoretical Overview and Recent Developments

8:10 AM	B. Johansson, "Magnetic, Structural and Electronic Relationshipsbetween the Lanthanide and Actinide Elements"
8:50 AM	G. Kotliar, "Dynamical Mean Field Theory of Elemental Plutonium"
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Magnetic, Structural and Electronic Relationships between the Lanthanide and Actinide Elements

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The similarity and difference between the solid state properties of the 4f and 5f transition metals are pointed out. The later 5f elements show properties which have direct correspondence to the early 4f transition metals, suggesting a localized behaviour of the 5f electrons for those metals. The fact that Pu metal has a 30% lower volume than its neighbour heavier element, Am, suggests a tremendous difference in the properties of the 5f electrons for this element relative to the heavier actinides. This change in behaviour can be viewed as a Mott transition as a function of the atomic number Z. On the metallic side of the Mott transition, the elements show most unusual crystal structures, the common feature being their low symmetry, and relatively inefficient filling of space. An analogous behaviour for the lanthanides is found in cerium metal under compression, where structures typical for the light actinides have been found experimentally. A generalized phase diagram for the actinides is shown to contain features comparable to the individual phase diagram of Ce metal. The crystal structure behaviour of the lanthanides and heavier actinides originates from the number of 5d (or 6d) electrons in the metallic state. Electronic structure calculations account very well for the ground state crystal structures of the actinides. The distorted structures can be understood as Peierls distortions away from the symmetric bcc structure and originate from strongly bonding 5f electrons occupying relatively narrow 5f states.

Dynamical Mean Field Theory of Elemental Plutonium

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We will describe recent developments in the dynamical mean field theory (DMFT), an electronic structure method to treat correlated electron materials, and its application to elemental plutonium.

This approach gives a coherent qualitative picture of many physical properties of Pu. We will discuss quantitative results for the cohesive properties of the delta and epsilon phases, and compare our results against experiments and alternative theories.

Thermodynamic and spectral properties of compressed Ce calculated by the merger of the local density approximation and dynamical mean field theory

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We have calculated thermodynamic and spectral properties of Ce metal over a wide range of volume and temperature, including the effects of 4f electron correlations, by the merger of the local density approximation and dynamical mean field theory (DMFT). The DMFT equations are solved using the quantum Monte Carlo technique supplemented by the more approximate Hubbard I and Hartree Fock methods. At large volume we find Hubbard split spectra, the associated local moment, and an entropy consistent with degeneracy in the moment direction. On compression through the volume range of the observed gamma-alpha transition, an Abrikosov-Suhl resonance begins to grow rapidly in the 4f spectra at the Fermi level, a corresponding peak develops in the specific heat, and the entropy drops rapidly in the presence of a persistent, although somewhat reduced local moment. Our parameter-free spectra agree well with experiment at the alpha- and gamma-Ce volumes, and a region of negative curvature in the correlation energy leads to a shallowness in the low-temperature total energy over this volume range which is consistent with the gamma-alpha transition. As measured by the double occupancy, we find a noticeable decrease in correlation on compression across the transition; however, even at the smallest volumes considered, Ce remains strongly correlated with residual Hubbard bands to either side of a dominant Fermi-level structure. These characteristics are discussed in light of current theories for the volume collapse transition in Ce.

Session II: Photoelectron Spectroscopy of Pu and Pu Materials

10:30 AM	T. Gouder, "5f Localization in Ultrathin Pu Layers"
11:10 AM	J. Joyce, "Electronic Structure of Pu and Pu Compounds from PES"
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1:00 PM	J. Tobin, "A New Paradigm for the Determination of 5f Electronic Structure using Spin-Dependent Photoelectron Spectroscopy"
1:40 PM	G. van der Laan, "Core-level photoemission spectra as a tool to assess the 5f electron localization of alpha and delta-like Pu"

5f Localization in Ultrathin Pu Layers

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Being right at the localisation threshold, Pu has an especially interesting position within the actinide series. The 5f electrons are only weakly itinerant, and a slight modification of the chemical environment may push them into localization. In particular, gradual transition of the 5f states towards localization can be observed, when confining Pu into thin films with decreasing thickness, where the coordination is suppressed.

Deposition of Pu on a single crystalline Mg substrate allowed to prepare pure Pu layers with controlled thickness down to 1 monoatomic layer, only weakly interacting with the substrate. High-resolution UPS and Pu-4f core-level spectra demonstrate the dramatic changes of electronic structure for Pu below 5 monolayers (ML) thickness [1]. For the "thick" layer (5 ML) a spectral intensity increasing up to the Fermi level cut-off, and representing the 5f conduction band, was observed. At reduced thickness (1 ML) this "triangular" peak is replaced by a new feature around 1.7 eV below EF. This broad maximum is also of 5f origin, and corresponds roughly to the 5f emission found in PuSb. Therefore we interpret it as due to the emission from 5f states, which get localized due to the reduced Pu coordination number. At intermediate thicknesses (2-3 ML), a three peaks structure of 5f character appears, showing 5f electrons in a quasi-localized state.

The apparent sensitivity of the electronic structure of Pu to coordination is also at the origin of a surface reconstruction on a-Pu. The valence band spectra of a-Pu, prepared by ion-etching at various temperatures, show a systematic evolution from the triangular (itinerant) form, characteristic for low-T surface preparation, into the d-Pu type, with 3 peaks close to EF, obtained at elevated temperatures. This supports the theoretical conjecture [2] that the surface of a-Pu should have a d-Pu character.

Electronic Structure of Pu and Pu Compounds from Photoelectron Spectroscopy

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A comparison between the measured photoemission spectra and various computational schemes for the delta phase of Pu metal reveals a wide range of mechanisms for treating the inherent complexities of plutonium electronic structure. Photoemission data for Pu metal along with results from single crystal compounds including PuIn3, PuSb2, PuCoGa5 and PuSn3, reveals systematics in the bonding and hybridization of the 5f electrons with the conduction states. Outside of the scope of a general Pu electronic structure scheme are the Pu compounds PuSb and PuTe which show localized characteristics. Photoemission results for several photon energies allow a separation in the valence band spectra between hybridized and localized 5f states. The variation in spectral intensity as a function of temperature between 10 and 300 K for peaks near the Fermi level indicates narrow band as opposed to many-body resonance characteristics. Exposure of clean surfaces to molecular hydrogen and oxygen is used to separate surface and bulk contributions to the electronic properties. In the layered compound PuSb2 a peak at the Fermi level (70 meV wide) exhibits predominant 5f content while delta phase Pu shows a peak ~100 meV wide with a strong 6d admixture. A comparison between photoemission and the mixed level model (constrained generalized gradient approximation calculations) is presented as this computational approach has been extended to include compounds of Pu as well as elemental phases.

A New Paradigm for the Determination of 5f Electronic Structure using Spin-Dependent Photoelectron Spectroscopy

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Despite recent intensive experimental effort [1-3], the electronic structure of Pu, particularly δ-Pu, remains ill defined. An evaluation of our previous synchrotron-radiation-based investigation of α-Pu and δ-Pu [1] has lead to a new paradigm for the interpretation of photoemission spectra of U, Np, α-Pu, δ-Pu and Am. This approach is founded upon a model in which spin and spin-orbit splittings are included in the picture of the 5f states [4] and upon the observation of chiral/spin-dependent effects in non-magnetic systems. [5,6] By extending a quantitative model developed for the interpretation of core level spectroscopy in magnetic systems [7], it is possible to predict the contributions of the individual component states within the 5-f manifold. This has lead to a remarkable agreement between the results of the model and the previously collected spectra of U, Np, Pu and Am, particularly δ-Pu, [1-3,8] and to a prediction of what we might expect to see in future spin-resolving experiments. [9] This work was performed under the auspices of the U.S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

*Collaborators: B.W. Chung, LLNL; R.K. Schulze, LANL; D.K. Shuh, LBNL

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8. J.R. Naegele, "Photoem. of Solids," Landolt-Bornstein **III/B,**183 (1994).

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Core-level photoemission spectra as a tool to assess the 5f electron localization of alpha and delta-like Pu

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Results of Anderson impurity calculations will be presented for alpha and delta Pu and thin films of Pu with different thicknesses and compared to recent experimental results. The 4f core-level photoemission spectra display a screened and an unscreened peak that can be used to measure for the degree of localization. An increased localization (more atomic-like) leads to decreased overlap which leads to a volume increase.

The physics of f electron systems at finite temperature is dominated by the phenomenon of f electrons fluctuating between different configurations. This has been impossible so far to include in the electronic methodology of a one-electron mean-field description. Pu is considered to be the most complex and anomalous elements in the periodic table. The phase diagram of Pu metal has seven allotropes, some with very complex crystal structures not found in other metals, such as alpha-Pu (the low-temperature phase) which has a complex monoclinic structure, whereas on the other hand delta-Pu has a simple face-centered cubic (fcc) structure. The delta-phase which is stable at ambient pressure and around 600 to 700 K has a 25 % larger atomic volume than the alpha-phase.

There is a competition between localization (electron-electron interaction) and delocalization (kinetic energy). The many-body crystal wavefunction has to reduce to many-body atomic wavefunctions as lattice spacing is increased. Such a strongly correlated electrons system can be tackled by Anderson impurity model or dynamical-mean field theory. In these models intra-atomic Coulomb interaction and hybridization are considered at the same footing. Correlation effects depend on the lattice phase. For instance, when the distance between the atoms is small, the correlation effects may not be so important, since the hybridization, and consequently the bandwidth becomes large.

Session III:

Poster Viewing with Refreshments

Fermi surface studies of actinide compounds via positron annihilation experiments.

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The measurement of the 2-dimensional angular correlation of the positron annihilation radiation (2D-ACAR), providing a 2D projection of the two-photon electron-positron momentum density, r{p}, is a powerful tool to investigate the electronic structure of intermetallic compounds. Utilising tomographic reconstruction techniques, the experiment has the unique ability to sample the **k**-space density of truly 3-dimensional systems in a cartesian mesh and yield information on their Fermi surface (FS).[1,2] We have investigated the character of the 5f electrons in the two actinide-based antiferromagnets, USb and UGa_3.

1) The monopnictide semimetal USb differs from the monopnictides UN, UP and UAs for the much lower density of states at the Fermi level and a triple-**k**, non collinear, magnetic structure. The 2D-ACAR **k**-space occupancy projected along the high symmetry [100] direction turns out to be very similar to that of the isostructural, 4f monopnictide, CeSb [3]. Moreover, the experimental spectrum shows a fair agreement with the results of a full potential band structure calculation in local density approximation (FLAPW-LDA) which treated the f-degree of freedom as localized (f-core). The 3d reconstruction of the **k**-space density, obtained utilizing a total of four projections, suggests that the features of the [100] projection are due to small hole-like and electron like FSs centred at the centre (G) and at the borders (X) of the BZ, respectively. This result is consistent with the predictions of the f-core model and with the semimetallic properties of USb. At the moment we are investigating the slight discrepancies between experiment and f-core model by including the e-p matrix elements in momentum density and **k**-space density calculation. Further studies on the differences observed in the experimental spectra across the paramagnetic-antiferromagnetic transition are under way.

2) We show preliminary results of our measurements on the heavy fermion antiferromagnet UGa_3, performed across the antiferromagnetic transition. Confirming previous discrepancies between experiments and theory [4], the experimental data cannot clearly be interpreted by standard band structure calculations where the f-degree of freedom is either treated as itinerant or localized. Therefore, our results do not fully confirm the standard assumption of UGa_3 as the { archetype} itinerant antiferromagnet.

[1] G Kontrym-Sznajd and E. Jozefczuk, Mat. Scie. Forum 255-257, 754 (1997) and references therein.
[2] D.G. Lock, V.H.C. Crisp and R.N. West, J. Phys. F 3, 561 (1973)
[3] F. Itoh, H. Sakurai, T. Chiba, T. Akahane, T. Suzuki and Y. Kubo, Physica B 186-188, 169 (1993)
[4] D. Aoki et al., J. Phys. Soc. Japan 70, 538 (2001)

Investigating the Delta/Alpha-Prime Martensitic Phase Transformation in Pu-Ga Alloys

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The alpha-prime/delta martensitic phase transformation in Pu-Ga alloys is unusual and is not well understood. This transformation exhibits a large temperature hysteresis and the maximum amount of alpha-prime formed is approximately 30%. Here, we report the development of experimental techniques for investigating the stability and transformation of Pu-Ga alloys. Because the resistivities of the alpha-prime and delta phases differ significantly, four-point probe resistometry is an effective and sensitive technique for monitoring the transformation. Initial resistometry results from thermal cycling of a 2 at% Pu-Ga alloy demonstrate a reproducible transformation hysteresis. The alpha-prime phase begins to form at 160 K and reversion to delta begins at 320 K. Isothermal quench experiments suggest that, at some temperatures, there may be an "incubation period" before alpha-prime begins to form. Differential scanning calorimetry (DSC) will soon be used to further investigate the thermodynamics and kinetics of the transformation. Initial DSC results from a martensitic transformation in a shape-memory alloy are discussed.

Photoemission of UCoGa5 and PuCoGa5

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Photoelectron spectroscopy (PES) studies have been carried out on the pair of compounds UCoGa5 and PuCoGa5 in order to determine the details of their electronic structure. While PuCoGa5 is a superconductor with a TC of 18K, and a gamma value of 77 mJ/moleK2, the Uranium counterpart shows neither significant magnetic nor enhanced mass characteristics. We present initial angle-integrated PES measurements for both the Uranium and Plutonium based compounds taken at photon energies accessible with a Helium lamp. The Pu compound results lean towards the characteristics of its Cerium counterpart, CeCoIn5 (one of the Ce based family of heavy fermion superconductors), with significant electron correlations requiring a description beyond the one-electron approximation. We also present angle-resolved measurements for UCoGa5 taken on the PGM beamline at the SRC in Wisconsin. High quality single crystal samples were used, as confirmed by Laue patterns, and the band structure investigated along several directions at T~10 K. Measurements were taken over a wide energy range encompassing the maximum variations in Co 3d vs. U f-electron cross-sections with any overall energy resolution for the lowest photon energy of the order of 20mV. The behaviour of the observable peaks within 2 eV of the Fermi energy in normal incidence data do not follow simple photoelectron cross-sectional arguments suggesting a considerable degree of hybridization of the 4f electrons. A comparison to density functional theory calculations within the GGA framework is made with the PES results with the successes and shortcomings of the comparison detailed. Work supported by the U.S. DOE OBES

Photoelectron Spectroscopy of Plutonium at the Advanced Light Source

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We are developing a program to perform Photoelectron Spectroscopy and X-Ray Absorption Spectroscopy upon highly radioactive samples, particularly Plutonium, at the Advanced Light Source in Berkeley, CA, USA. First results from alpha and delta Plutonium [1] are reported as well as plans for a dedicated spectrometer for actinide studies. [2]

1. J. Terry, R.K. Schulze, J.D. Farr, T. Zocco, K. Heinzelman, E. Rotenberg, D.K. Shuh, G. van der Laan, D.A. Arena, and J.G. Tobin, Surface Science Letters **499**, L141 (2002).
2. J. Tobin, D.A. Arena, B. Chung, P. Roussel, J. Terry, R.K. Schulze, J.D. Farr, T. Zocco, K. Heinzelman, E. Rotenberg, and D.K. Shuh, "Photoelectron Spectroscopy of Plutonium at the Advanced Light Source", UCRL-JC-145703, J. Nucl. Sci. Tech./ Proc. of Actinides 2001, accepted 2002.

Photoemission studies of AnSb and AnTe single crystals (An = Np, and Pu)

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We have performed photoemission experiments, both with the HeI (21.2 eV) and HeII (40.8 eV) and the laser plasma light source (LPLS) giving energies in the range 40 to 80 eV, on laser-cleaned surfaces of single crystals of the AnSb and AnTe series. This extends earlier work , allows us to study the systematics of the electronic structures of these compounds.

In all cases there is at least one strong peak in the photoemission spectra that can be identified from its energy dependence as associated with the main spectral weight of the 5f states. The distance of this peak from EF (all in eV) is: USb 0.2; NpSb 0.7; PuSb 1.7; UTe 0.8; NpTe 1.3; PuTe < 0.1. The compound that shows the greatest localization is therefore PuSb, and the most unusual is PuTe, where there are at least three peaks within the first 1.2 eV below EF. The results for PuTe and PuSb agree well with those published [4] for PuSb and PuSe using thin films. This demonstrates that the spectra are independent of the cleaning or surface preparation. The energy dependence, established by using the LPLS, also confirms that all features within 2 eV of EF have a predominant 5f character. Thus the sharp (often small, except for the case of PuTe) features at EF are also a measure of the 5f spectral weight, even if there is hybridization with the conduction states.

Interestingly, although the AnSb compounds show an increased localization from U to Np to Pu (as might be expected from their magnetic properties), the situation is quite different for the AnTe compounds. Initially NpTe is more localized than UTe, but the PuTe shows a rich spectrum, which, as in the case of PuSe [4], cannot be reproduced by any current models.

The electronic structure of USb2 investigated by angle-resolved photoemission

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We have studied single crystal antiferromagnetic USB2 by angle-resolved photoemission with synchrotron radiation in the photon energy range of 20-110 eV. The overall energy resolution for lowest photon energy range was 20 meV, and the momentum resolution was 0.09A-1, which is better than previous USb2 data [1]. The high quality of the sample was confirmed by Laue patterns and by a sharp photoemission peak near the Fermi level (EF).
Photoemission spectra measured for photon energies of 34eV, 43 eV and 60 eV showed two structures with binding energies between 0 and 1 eV below EF: a very sharp peak labeled A (full width at half maximum (FWHM) 30-50 meV) is situated within 100 meV of EF and a broader peak labeled B is (FWHM 220-240 meV) observed between 400 and 550 meV in normal emission spectra.
From cross-sectional arguments and resonant photoemission measurements taken near the U5d-U5f absorption edge, it can be confirmed that both A and B structures have mixed conduction electron/U 5f character indicating hybridization. Dispersion is observed for both structures A and B. The dispersion of B is around 200 meV in the Gamma-X direction, so it can be easily observed in the spectra. The excellent photon energy and momentum resolution allow for observation of dispersion in peak A, which was determined to be 14 meV along Gamma-X direction of the Brillouin zone.
The are many similarities in the photoemission between CeSb2 (ferromagnetic) and USb2 which suggest that the same theoretical model might be used to describe these two kinds of magnetic systems. The dispersion of U5f bands requires a theoretical models which accommodates band-like behavior of 5f electrons, such as the Periodic Anderson Model [2], though many other models may also be suitable for these magnetic materials.

5f- and 3d-Metals without Self-Interactions

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Omission of the artificial self-direct and self-exchange interactions of Local-Density Theory simplifies the understanding of the electronic structure of the actinides. It leads to "low" f-shell energy bands, partly occupied, and empty "high" f-shell energy bands. It reduces the bonding force of the f-shell electrons and may, or may not, produce local moments. It also predicts a high density of states (and resulting large low-temperature specific heat) and a large temperature-independent paramagnetic susceptibility. The same theory applied to the 3d-transition elements makes understandable the complex behavior of alloys in the Pauling-Slater curve, a plot of saturation magnetization versus electron-to-atom ratio.

Magnetic Properties of Pure and Alloyed Plutonium metal.

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The physical properties of pure plutonium metal in its different phases and plutonium stabilized in the delta-phase by alloying (PuCe, PuAl, PuGa and PuAm) are at the origin of many questions concerning its electronic structure, especially the 5f electron states. At and below room temperature, pure Pu crystallizes in the alpha-phase (monoclinic), stable from 0 K to 395 K, while the delta-phase (fcc) is stable from 592 to 724 K. Four other allotropes are also present in the phase diagram before the liquid state (beta, gamma, delta prime and epsilon). The interest, however, has focussed on the alpha and delta-phases. The delta-Pu presents a higher localization for the 5f electron states than the alpha-Pu, as suggested by to the very large volume change between the two phases (24 %). In this paper we will present new magnetic susceptibility results on pure plutonium metal in its different allotropic phases as well as on different stabilized delta-Pu alloys . It is found in particular that, surprisingly enough, alpha and delta plutonium have the same susceptibility, while their electronic specific heat changes by a factor of two [3]. Only in the case of PuAm alloys the magnetic susceptibility follows clearly a Curie-Weiss law at low temperature. These results will be compared to already published data and discussed within the available models.

Effects of local solute ordering and plasticity on the delta to alpha transformation in gallium stabilized plutonium alloys

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The delta to alpha transformation in Ga-stabilized plutonium alloys has many unusual features. It is a thermally activated martensitic transformation with double-c transformation kinetics. The alpha product has an approximately 20% smaller volume than delta, but its volume can change an additional 2% depending on the transformation path. The thermally induced transformation also rarely proceeds to more than 40% completion. We use ab-initio techniques to look at local ordering of gallium in the alpha phase and use continuum elasto-plastic energy calculations to understand the possible effects of plastic deformations during the transformations. We discuss how local ordering and plastic deformation may explain some of the unusual features of the transformation. This work was performed under the auspices of the U.S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

Density-Functional Study of Magnetism in delta-Pu and its Alloys

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The Korringa-Kohn-Rostoker method within a Green's function formalism has been used to study delta-Pu and its dilute alloys. The effect of compositional disorder, as well as magnetic moment disorder, was treated by means of the coherent potential approximation. Calculations have been performed for ferromagnetic (FM) and antiferromagnetic (AF) spin configurations, as well as for the state with local moment disorder (DLM) that represents a paramagnetic state (PM). While AF delta-Pu remains mechanically unstable with respect to a tetragonal distortion at low temperatures, PM delta-Pu is stabilized at higher temperatures where disordered magnetic moments are present. Addition of small (10 at. %) amount of Ni, Al, Ga, Sc, Am, Ce, Th and Ac helps to lower the total energy of the PM phase with respect to the AF phase and thereby stabilizing delta-Pu to lower temperatures. This effect is most pronounced for elements, which size exceeds the size of Pu, e.g. Ce, Am, Th, and Ac. On the other hand, magnetic 3d transition metals, which size is smaller than size of Pu, e.g. Mn, Co and Fe, destabilize delta-Pu.

Multi-Scale Structural Study of the delta to alpha Transformation in a Pu-Ga Alloy

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Extended x-ray absorption fine structure spectroscopy (EXAFS) and optical microscopy were used to investigate changes in the grain morphology and in the local atomic environment of plutonium and gallium atoms through the martensitic delta to alpha transformation in a Pu-Ga alloy. The high-temperature fcc delta-Pu phase is stabilized at room temperature by the addition of a few at% of Ga. Upon cooling, the delta-Pu phase reverts to the Ga-insoluble, monoclinic alpha phase. Prior to the EXAFS experiments, a 2 at% Ga-doped delta-Pu sample was quenched to transform partially to alpha -Pu, while a second identical sample was left untransformed. Optical microscopy revealed alpha particles present in the quenched sample. EXAFS results measured at low temperature compare the structural behavior of the pre-transformed and untransformed samples. EXAFS spectral components attributed to both alpha-Pu and delta-Pu were observed in the partially transformed sample, and Pu and Ga EXAFS spectra indicate similar local atomic environments, suggesting Ga is substitutional for Pu atoms in both the alpha-Pu and delta-Pu structures. EXAFS also is used to separate the thermal dependence of the local bonding in each of the phases in the partially transformed alloy.

This work was performed under the auspices of the U.S. Department of Energy by University of California Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48, under LDRD funding. Portions of this research were carried out at the Stanford Synchrotron Radiation Laboratory, a national user facility operated by Stanford University on behalf of the U.S. Department of Energy, Office of Basic Energy Sciences.
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OPPORTUNITIES IN SOFT X-RAY SYNCHROTRON RADIATION FOR ACTINIDE SCIENCE

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Synchrotron radiation (SR) methods have been utilized with increasing frequency over the past several years to study scientific issues in actinide science, ranging from those of a fundamental nature to those that address a specifically-targeted technical need. The actinide research community has been able to capitalize on SR methodologies for investigations of radioactive materials because of improved radiological safety infrastructure, progress in detector technology, and the capability to perform experiments with small amounts of actinide material. In particular, the emergence of microspectroscopic and fluorescence-based techniques have enabled investigations of actinide materials at sources of soft x-ray SR. The results from several soft x-ray SR investigations of actinides performed at the Advanced Light Source(ALS) at Lawrence Berkeley National Laboratory (LBNL) will be presented including near-edge x-ray absorption fine structure and x-ray emission spectroscopy (XES) studies from several uranium materials systems. The characteristics and potential of the new ALS elliptically-polarizing undulator Beamline 11.0.2 for future actinide investigations will be highlighted.

This work was supported by the Director, Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences of the U.S. Department of Energy at LBNL under Contract No. DE-AC03-76SF00098.

Construction of a Novel Device for the Investigation of Actinide Nano-Science

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Predicting the aging behaviors of actinide materials is an interesting problem requiring advances in both theoretical understanding and experimental observation. This work seeks to determine the various correlation contributions active in actinide elements through observations of structural and electronic evolution in these materials as a function of particle size. Results from these experiments will be used to confirm the several proposed theoretical descriptions of these materials. The measurements (which will include XPS, UPS, AES, LEED, STM, and AFM) will be carried out on a number of different uranium and plutonium systems such as single crystalline nanoparticles and 1-D wires produced via Pulsed Laser Deposition (PLD). The ability of PLD to easily form nano-scaled material affords a great experimental opportunity to examine the development of size related parameters such as Coulomb energy, electron exchange energy, spin orbit coupling, and crystal field effects. Photoemission and bandmapping studies as a function of nanoparticle size could allow the experimental determination of these effects to guide the development of the band structure theory. The current phase of the work involves the construction of a facility for the in situ growth of the nanoparticles and the suite of analytical instrumentation mentioned above. The apparatus will be required to maintain an aggressive UHV environment(10^-11 to 10^-12 Torr) while still maintaining the flexibility to carry out the objectives listed above. The bulk of the analysis chamber has been completed, with XPS, UPS, and AES capabilities currently available. The portable ablation "suitcase" is also nearing completion along with the sample handling and transfer systems.

Atomistic Modeling of Defect Production and Annealing in PuGa

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Radiation damage, including the self-induced damage of alpha decay, can significantly alter material microstructure and a wide range of material properties. Microstructural evolution results from the generation of primary damage in spatially correlated high-energy displacement cascades and the subsequent diffusion, clustering and long-range transport of vacancy and self-interstitial defects. A key to understanding and predicting radiation damage and its attendant consequences is developing fundamental knowledge of both primary defect production and the defect diffusion and clustering kinetics. Low temperature proton irradiation, as well as in-situ self-irradiation, and isochronal annealing experiments performed on the same PuGa alloy provide key information on defect kinetics through the identification of annealing recovery stages, which are influenced by the signature of the primary damage source term. By closing coupling these experiments to atomistic modeling, we are able to obtain fundamental understanding of both the primary damage production and the defect kinetics. The atomistic modeling consists of molecular dynamic (MD) simulations of primary damage production and kinetic Monte Carlo (KMC) modeling of the subsequent defect evolution through the isochronal annealing protocol. Semi-empirical potentials that accurately describe Pu or PuGa alloys do not currently exist and, thus low melting temperature, face centered cubic (fcc) metals have been used as surrogates both in MD simulations of primary defect production and in the kinetic transport and clustering database for the KMC simulations. A single set of simulation parameters captures the differences between the experimental annealing recovery spectra of proton and self-irradiated PuGa. Finally, the experimentally validated radiation damage source term and defect kinetics provide the basis for predicting the long term aging behavior of plutonium alloys.

This work was performed under the auspices of the U. S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

Session IV:
Resistivities and Susceptibilities

4:00 PM	J.-M. Fornier, "Magnetic properties of PuAm solid solutions : evidence for a Curie-Weiss behavior and aging effects"
4:40 PM	L. Havela, "Non-Fermi Liquid Behavior in a Band Metamagnet UCoAl"
5:20 PM	M. Fluss, "Temperature Dependent Properties of Defects from Ion-Irradiation in Pu(Ga)"

Magnetic properties of PuAm solid solutions : evidence for a Curie-Weiss behavior and aging effects

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As other elements such as Ga, Al or Ce, Am allows to stabilize at room temperature the high temperature face centered cubic delta-phase of pure Pu. However, the mechanisms for delta-phase stabilization, which might be strongly related to the electronic properties of these Pu solid solutions, remain unclear. In the present work, magnetic and electric measurements were then performed on several delta-PuAm solid solutions (4.9 at.% < Am content < 43 at.%) in order to better understand the electronic properties of these alloys. Changes in magnetic susceptibility versus temperature (300 K down to 4 K) show a Curie-Weiss behavior which allows to determine the effective magnetic moment of Pu atoms [mu-eff(Pu)]. A sharp increase in mu-eff(Pu) occurs for an Am content of 24 at.%. This transition is confirmed by electrical resistivity measurements. This could be explained by the presence of a Kondo effect, below 24 at.% of Am content, which might be suppressed above 24 at.% by the localization of the Pu 5f electrons. Moreover, measurements were performed on one year old solid solutions, which means that the samples contained many self-irradiation defects such as vacancies, interstitials and clusters of these. For all the PuAm solid solutions studied, a strong increase in the magnetic susceptibility is observed at low temperature (T < 75 K) for magnetic fields lower than 4.5 T. A similar anomaly, which is not explained yet, is also observed on aged delta-PuGa solid solutions and decreased after a heat treatment. A tentative explanation, based on molecular dynamics calculations, is given.

Non-Fermi Liquid Behavior in a Band Metamagnet UCoAl

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A lot of attention has been recently devoted to details of the onset of magnetic ordering in intermetallic systems. Particularly interesting are systematic deviations from the standard Fermi liquid behaviour of basic transport and thermodynamic properties, which can be sorted out into several universality classes. This so called Non-Fermi liquid (NFL) behaviour is often achieved by using doping as a main control parameter. The resulting atomic disorder can unfortunately bring undesirable effects related to statistical distributions of important parameters. Therefore if is important to orient on materials, in which NFL behaviour exists without any doping.

UCoAl is an ordered ternary intermetallic compound, which does not undergo magnetic ordering, as the U 5f states are rather strongly hybridized with electronic states of ligands. The proximity to the onset of magnetic ordering is manifest in a step-like metamagnetic transition, which induces moments of 0.3 Bohr magneton per formula unit. The phenomenology of the metamagnetism in UCoAl indicates a similarity with the so called band metamagnets of the YCo2 type. The critical field (0.65 T) is relatively very low and allows an easy study of the variations of electronic properties across the transition. In particular, we found that the NFL scaling of electrical resistivity with exponent $n = 5/3$ appears in the non-magnetic state, whereas the standard $n = 2$ is restored above the metamagnetic transition. UCoAl thus represents a new type of undoped material, which combines NFL behaviour with a band metamagnetism. Experiments under hydrostatic pressure indicate that NFL characteristics are relatively robust, which contradicts the general intuition that NFL behaviour appears in the close vicinity of a quantum critical point.

Temperature Dependent Properties of Defects from Ion-Irradiation in Pu(Ga)

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We report on the restively measured isochronal annealing Dr(T)/r_0 and temperature dependence of the resistivity, r(T), of annealed defect populations resulting from low-temperature (10K to 20K) accumulated ion-damage in the stabilized delta-phase of Pu(3.3 at%Ga). Annealing curves for self-irradiation from the alpha decay of plutonium and from 3.8 MeV proton irradiations were measured and compared with combined molecular-dynamics and kinetic-Monte-Carlo simulations (MD-KMC). The low-temperature differences in the annealing properties are understood as a consequence of the source-term differences from these two very different types of ion-damage. In particular, the spatially compact damage cascade resulting from the uranium recoil of the alpha particle results in extended interstitial defect clusters which are not possible for the proton irradiation. Damage populations resulting from low-temperature (10K) damage-accumulation were annealed at specific temperatures (30K, 150K and 250K) producing intermediate defect populations. The specific resitivity of the defects was found to vary by a factor of eight from 150K to 10K. The temperature dependence, r(T), of the vacancy dominated defect populations (150K and 250K) follows a r(T) = – a*ln*(T)+b dependence suggestive of a Kondo-like magnetic impurity (1) at vacancy defect sites. If true, the consequences of this observation could be profound, suggesting that the implied 5f localization in the neighborhood of vacancies and other dilations in the lattice results in localized magnetic behavior, reduced metallic bonding, and hence might be the structure-property relationship or *impurity* that precipitates a more global electronic structure change leading to the "stabilization" of the delta-phase, as suggested by Cooper and co-workers (2).

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Session V: X-ray and Neutron Measurements, Analysis and Simulations

8:00 AM	N. Edelstein, "Interplay of the spin-orbit and crystal field interactions of fn ions in crystals"
8:40 AM	G. Lander, "NpO2 : resonant x-ray scattering casts new light on an old problem"
9:20 AM	K. McEwen, "Quadrupolar and magnetic phase transitions in UPd3"
10:00 AM	Break
10:30 AM	M. Brooks, "Theory of Ground State Spin and Orbital Moments with Screened Exchange Interactions"
11:10 AM	L. Soderholm, "Correlated Electron Behavior in a Eu-exchanged W-O Cluster"

Interplay of the spin-orbit and crystal field interactions of fn ions in crystals

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The optical spectra of 4f1 and 5f1 compounds depend on the relative strengths of the spin-orbit and the crystal field interactions. For an octahedral crystal field, it is especially straightforward to separate out the effects. Examples will be given that illustrate the interplay between these two interactions. A special case occurs in for Oh symmetry in the case of the 5f5 ions, Pu3+ and Am4+. For these ions there is an inversion of the ground crystal field state due to the effects of intermediate coupling as compared to the corresponding lanthanide ion, Sm3+. The crystal field then mixes in excited states and from measurements of the ground state g values, information can be obtained about the magnitudes of the crystal field. Again examples will be discussed during the presentation.

NpO2 : resonant x-ray scattering casts new light on an old problem

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The mystery of what happens at To = 25 K in NpO2 is now 50 years old. The specific heat was published in 1953 and showed a large lamda-like anomaly at 25 K. It was assumed that this represented dipole magnetic order, especially as Np4+:5f3 is a Kramer's ion, and so the ground state cannot be a singlet. However, extensive neutron and Mossbauer (237Np) experiments failed to find any sign of a dipole moment, and studies have put a limit of ~ 0.01 μB/Np. Recent mSR experiments have shown a small precession signal indicating that time reversal symmetry is broken below 25 K.

Three years ago we published data showing that a resonant x-ray scattering (RXS) is present in NpO2 below To. However, we did not have the capability either to analyse the polarization of the scattered photons or to measure the intensity as a function of the azimuthal angle. In Feb. 2002 we repeated the study with these two capabilities.

The RXS scattering from NpO2 that occurs below To may unambiguously be identified as arising from the ordering of quadrupole moments. This identification will be explained. The experiment solves a 50-year old mystery. However, it raises another. The susceptibility and Mossbauer measurements show that the Kramer's degeneracy is lifted. The quadrupole ordering is even in <M> so cannot be responsible for this; one is therefore driven to suggest weak octupole ordering as well.

To our knowledge NpO2 is the only system so far in which a quadrupole transition is not accompanied by a dipole ordering at lower temperature. I will speculate how common this effect might be in the actinides, and the unique set of circumstances, including the interplay of orbital degrees of freedom, that may be responsible for this phenomenon

Collaborators include: J. A. Paixao, C. Detlefs, M. Longfield, R. Caciuffo, P. Santini, N. Bernhoeft, and J. Rebizant. The experiments were performed at the ESRF, Grenoble.

Quadrupolar and magnetic phase transitions in UPd3

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Quadrupolar ordering in a 5f electron system has been observed directly for the first time, using x-ray resonant scattering techniques [1]. In UPd3 at low temperatures, two sets of satellite peaks are observed; both sets show a resonant enhancement of the scattering at the MIV edge of U. The polarization dependence of the peaks was investigated as a function of temperature. These x-ray scattering measurements, combined with neutron scattering and bulk property studies reveal a total of 4 antiferroquadrupolar (AFQ) phases between 8K and 4K in UPd3. The lowest temperature phase is also very weakly antiferromagnetic.

The 5f electrons in UPd3 are well localised, and have the 5f2 configuration. Since the crystal structure is dhcp, U atoms are at sites with locally hexagonal and quasi-cubic symmetry, each having their own set of crystal field levels, which have been determined by inelastic neutron spectroscopy. We will discuss the order parameters of the AFQ phases, and develop a mean-field model which can explain how the various phase transitions arise.

Theory of Ground State Spin and Orbital Moments with Screened Exchange Interactions

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The local spin density approximation has produced remarkably consistent results for calculated spin densities and magnetic moments but fails when the orbital contribution to magnetism is important. We argue that the reason is due to the approximate treatment of exchange, which should be orbital dependent. As an alternative, exchange integrals for a screened Coulomb interaction of the Yukawa form (SCI) with the Thomas-Fermi wave vector expressed in terms of the total electron density have been calculated for the transition metals Fe, Co and Ni, the rare earth intermetallic CeFe2, the uranium intermetallic UFe2 and uranium sulphide. The aim is the determination of ground state spin and orbital moments for a range of materials across the periodic table,from a single theory with no adjustable parameters.

The SCI theory was incorporated into self-consistent relativistic LMTO codes. For Fe, Co and Ni the calculated spin and orbital moments are in excellent agreement with measurements except that the calculated orbital moment of Ni is a little large. For US the measured (neutron diffraction) magnetic amplitude and total moment are reproduced almost exactly - the calculated orbital and spin moments of 1.25 and -2.92 at the U site being somewhat less than in previously published results. For UFe2 the measured magnetic amplitude for the U site is reproduced to an accuracy better than the spread in experimental data. For CeFe2 the measured magnetic amplitude at the Ce site is also reproduced and this leads to a reinterpretation of the neutron diffraction data. The reason that previous interpretation of the neutron diffraction results is flawed appears to be that free atom calculations used in their interpretation yield incorrect densities for the solid in the intermetallics studied here. Comparison is also made with Compton scattering and XMCD data for the spin and orbital moments.

Correlated Electron Behavior in a Eu-exchanged W-O cluster

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The development of effective methodologies for including highly-correlated-electron interactions in theoretical descriptions of a material's electronic properties is proving a difficult challenge. Correlated electrons can strongly influence static and dynamic electronic responses as well as the conductivity and magnetic properties of materials. Correlation effects have been most extensively studied in intermetallic compounds and, more recently, in perovskite-related oxides. Evidence is presented herein that an electroactive heteropolyanion exhibits behavior consistent with the presence of highly-correlated electrons. Their well-defined cluster size, coupled with their unprecedented degree of tunability and diverse structures, make these nanosized clusters ideal for pursuing studies on correlated-electron interactions. This work is supported by the U.S. DOE /OBES, Chemical Sciences, under contract W-31-109-ENG-38.

Session VI: Pu Theory

1:00 PM	P. Soderlind, "Density-functional investigation of magnetism in delta-Pu"
1:40 PM	J. Wills, "A mixed-level model of orbital and spin correlation in actinide materials"
2:20 PM	Break
2:50 PM	B. Sadigh, "First-Principles Calculations of the alpha and delta phases in Pu and Pu-Ga"
3:30 PM	A. Kutepov, "The ab-initio magnetic moments of alpha-plutonium"

Density-functional investigation of magnetism in delta-Pu

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We present density-functional results of delta-Pu obtained from three electronic-structure methods. These methods have their individual strengths and are used in combination to investigate the magnetic and crystal stability of delta-Pu. An all electron, full potential linear muffin-tin orbitals (FPLMTO) method, that includes corrections for spin-orbit coupling and orbital-polarization effects, predicts delta-Pu to be an antiferromagnet (AF) at zero temperature with a volume and a bulk modulus in very good agreement with experiment. The site projected magnetic moment is small due to large cancellation of spin and orbital moments. These calculations also predict a mechanical instability of AF delta-Pu. In addition, techniques based on the Korringa Kohn Rostocker (KKR) method within a Green's functions formalism and a projector augmented wave (PAW) method predict the same behavior of delta-Pu. In order to study disordered magnetism in delta-Pu, the KKR Green's function technique was used in conjunction with the disordered local moment (DLM) model, whereas for the FPLMTO and PAW methods this was accomplished within the special quasirandom structure (SQS) model. While AF delta-Pu remains mechanically unstable at lower temperatures, paramagnetic (PM) delta-Pu is stabilized at higher temperatures where disordered magnetic moments are present and responsible for the crystal structure, the low density, and the low bulk modulus of this phase.

A mixed-level model of orbital and spin correlation in actinide materials

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We present calculations of actinide element and compound electronic structure based on the Mixed Level Model,(1) in which itinerant electrons (including f-states), treated within the LDA, coexist and interact with spatially localized N-electron multiplets, where N is a parameter chosen to minimize the total energy. Itinerant electrons provide bonding energy while multiplets provide correlation energy. The multiplet-itinerant electron interaction provides a width to the multiplet levels, a shift in spectral weight, and an energy shift. Calculations of structural properties and electronic spectrum of elemental Pu and Pu compounds will be presented.

First-Principles Calculations of the alpha and delta phases in Pu and Pu-Ga.

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The results of extensive first-principles density functional theory calculations will be presented which have been carried out within the generalized gradient corrected approximation of the alpha and delta phases of pure Pu and Pu-Ga alloys. We discuss the effect of spin polarization in stabilizing the delta-phase and examine the structural implications of various spin configurations.
For the alpha structure, full relaxation of the atomic coordinates has been carried out to arrive at the energetically most stable structure as predicted by DFT. Good agreement with the experimentally observed structure is obtained after correcting for thermal expansion.
We have further studied the vibrational properties of the alpha phase at finite temperatures. The MD results reveal interesting vibrational modes of structural groups of Pu atoms within the unit cell of the alpha phase.
Encouraged by the results obtained for the pure Pu phases, a comprehensive study was carried out for substitutional Ga in the two phases. We discuss the implication of these results on the stabilization of the delta structure through alloying with Ga, as well as the martensitic transformation to the alpha' phase.

The ab-initio magnetic moments of alpha-plutonium.

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In the recent work [1] the structural and magnetic properties of a few phases of plutonium have been investigated. The principal conclusions in the work [1] are:

- delta-plutonium has an antiferromagnetic ordering;
- the structural properties of delta-plutonium are reproduced exactly when taking into account the orbital polarization;
- alpha-plutonium is nonmagnetic at experimental volume.

The last conclusion is disputable however, because the conclusion of the work [2] is that the ground state of alpha-plutonium is a compensated antiferromagnet.

The given contribution is devoted to theoretical study of magnetic structure of alpha-plutonium. The density functional theory in generalized gradient approximation has been used. The calculations have been performed by the full potential, fully relativistic (i.e. solving the Dirac equation) spin polarized linear method of augmented plane waves (FSPRLAPW+LO). The local orbital (LO) [3] has been added to the basis. Because of the very complicated crystal structure of alpha-plutonium the fully relativistic calculations have been performed at experimental volume only. Three types of calculations have been carried out: ferromagnetic, antiferromagnetic and nonmagnetic. The antiferromagnetic calculation results in the lowest energy. Thus, the conclusion of the given work coincides with the conclusion from the work [2].

The influence of spin polarization on structural properties of alpha-plutonium has been studied in scalar-relativistic approximation. The result is that taking into account the spin polarization essentially improves the agreement of calculated equilibrium volume and bulk modulus with the experimental data.

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Session VII:

Workshop Summary and Discussion